



DEVELOPMENT OF A REAL-TIME MONITOR OF AIRBORNE BERYLLIUM FOR THE Y-12 NATIONAL SECURITY COMPLEX

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**Y-12 National Security Complex
Oak Ridge, Tennessee 37831
managed by
BWXT Y-12, L.L.C.
for the
U.S. Department of Energy
Under Contract DE-AC05-00OR22800**

OVERVIEW

- The Y-12 National Security Complex needs a portable, near-real-time monitor of airborne Be down to $<0.2 \mu\text{g Be/m}^3$ of air.
- “Near-real time” means that a low level of Be can be measured within a few minutes.
- A general monitor should be able to measure the Be of any Be compound, including BeO.
- Airborne Be might be present as BeO (b.p. of 3900°C), as Be metal (b.p. of 2970°C at 5 torr), or as other Be compounds.
- The temperature of the plasma generated from the laser pulse should be sufficient to evaporate, dissociate, and ionize the Be from BeO.

OVERVIEW (Cont'd)

- An aqueous suspension of BeO can be used to generate aerosol particles to test a given method.
- For example, when a suspension of sub-micron BeO particles was analyzed by ICP/AES using a cross-flow nebulizer and spray chamber, ~70% of the known concentration of Be in the BeO suspension was detected.
 - This indicated that the argon-ICP plasma was hot enough to vaporize, dissociate, and ionize the Be from BeO particles.
 - Some loss of BeO particles may occur between the nebulizer and the plasma torch.
 - Use of a direct-injection nebulizer might have yielded a Be concentration closer to 100%.

AEROSOL-FOCUSING LASER-INDUCED-BREAKDOWN SPECTROSCOPY

- The method proposed for Be-aerosol monitoring at the Y-12 Complex is aerosol-focusing laser-induced-breakdown spectroscopy.
- Aerosol-focusing LIBS, which was invented by M.D. Cheng (U.S. Patent Application #9,416,337, June 1999), employs a nozzle which concentrates the aerosol to a focal point where the plasma is formed by the laser pulse.
- Aerosol focusing gives a 3-fold increase in sensitivity.
- We have not yet measured Be by aerosol-focusing LIBS, however the minimum detection limit (MDL) will be estimated in the next two view graphs.

AEROSOL-FOCUSING LASER-INDUCED-BREAKDOWN SPECTROSCOPY

- Déjà vu, all over again, ~20 years later?
- In 1983, a MDL of $0.7 \mu\text{g Be/m}^3$ in air was determined at LANL using time-resolved LIBS with a 10-Hz laser at 1064 nm and ~200 mJ pulses for 100 seconds of data [Radziemski, L.J., *Anal. Chem.* **55** (1983) pp 1246-1252].
- Because aerosol focusing gives a 3-fold increase in sensitivity, adding this feature to the ~20-year-old LIBS technology could yield an MDL approaching $\sim 0.2 \mu\text{g Be/m}^3$ for 100 seconds of data.

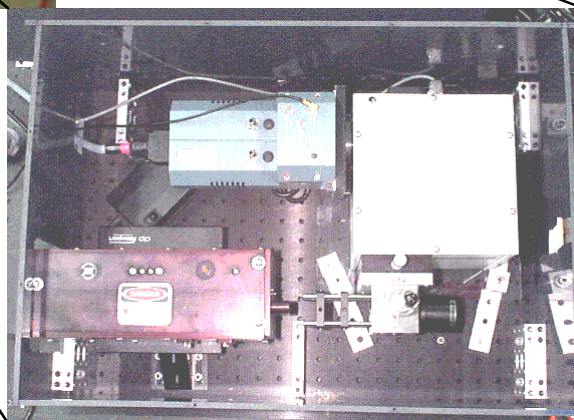
AEROSOL-FOCUSING LASER-INDUCED-BREAKDOWN SPECTROSCOPY

- With recent time-resolved aerosol-focusing LIBS at ORNL, airborne Cr has been measured down to a MDL of $\sim 0.4 \mu\text{g Cr/m}^3$ for 100 seconds of data. [Martin, M.; Cheng, M.D., *Applied Spec.* **54** (2000) 1279-1285.]
- With recent time-resolved LIBS by Fisher et al., the MDL of Be was found to be 3-times lower than the MDL of Cr (10 vs 30 $\mu\text{g/m}^3$) [Fisher, B.T., et al. *Applied Spec.* **55** (2001) pp 1312-1319.]
- Using this ratio, the aerosol-focusing LIBS at ORNL can be estimated to yield a MDL approaching $\sim 0.1 \mu\text{g Be/m}^3$ for 100 seconds of data.

AEROSOL-FOCUSING LASER-INDUCED-BREAKDOWN SPECTROSCOPY

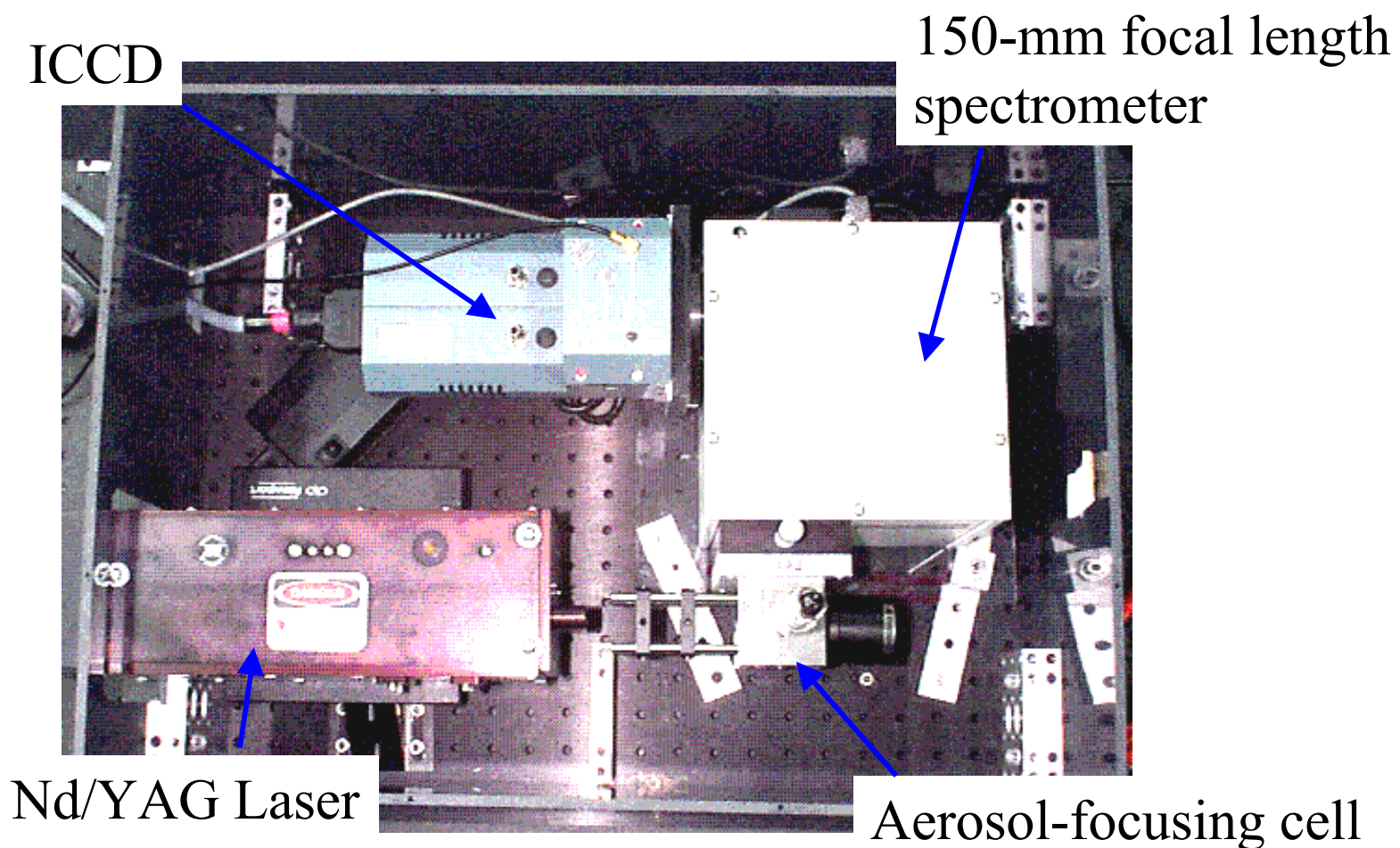


Portable unit enables in-situ measurement of the elemental composition of airborne particulate matter in near-real time.



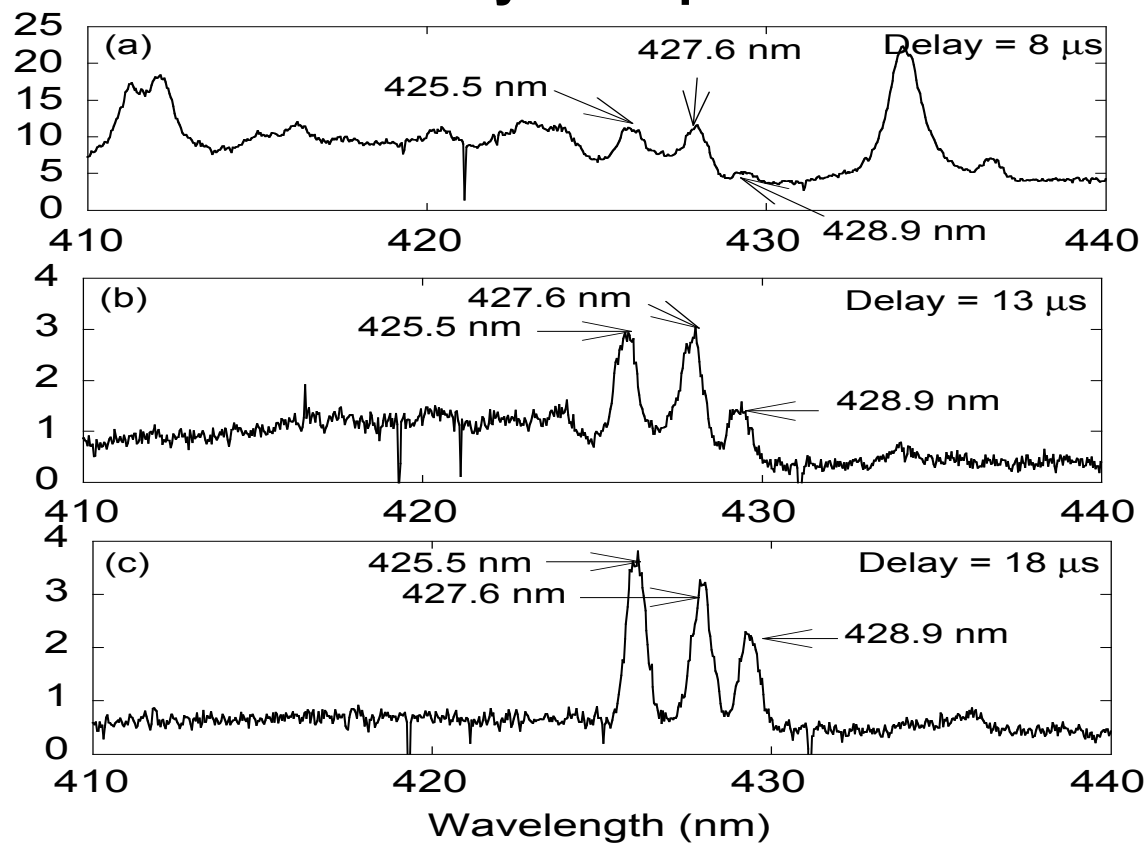
Instrument has a capability for the simultaneous, multi-element analysis of airborne particles.

AEROSOL-FOCUSING LASER-INDUCED-BREAKDOWN SPECTROSCOPY



AEROSOL-FOCUSING LASER-INDUCED-BREAKDOWN SPECTROSCOPY

Time-delayed acquisitions



(Background Corrected) $\times 10$

AEROSOL-FOCUSING LASER-INDUCED-BREAKDOWN SPECTROSCOPY

THE PARAMETERS OF PAST Cr WORK AT ORNL:

- Spectra from 10-Hz laser pulses co-added for 100 seconds
- 120-mJ laser pulses (~ 5 -nsec width) at 532 nm
- 5 L/min of sampled air
- 14- μ sec delay time and 20- μ sec gate time on ICCD detector

POSSIBILITIES TO ENHANCE SENSITIVITY:

[First investigate MgO (b.p. 3600 °C), then BeO (b.p. 3900 °C)]

- Use 30-Hz laser pulses (1000 pulses in ~ 33 secs)
- Compare laser wavelength of 355 nm to 532 nm
- Optimize times and emission wavelengths per element
- Consider additional emission wavelengths (for selectivity)

AEROSOL-FOCUSING LASER-INDUCED-BREAKDOWN SPECTROSCOPY

SUMMARY AND PLANS

- The Be monitor, being developed for the Y-12 National Security Complex, will need to measure airborne BeO.
- The LIBS method is expected to be sufficiently robust to measure Be in BeO (or Mg in MgO).
- The aerosol-focusing LIBS instrument is predicted to have a MDL of $\sim 0.1 \mu\text{g Be/m}^3$ for 100 seconds of data.
- Studies will be initiated with MgO particulate to investigate potential improvements in general sensitivity.
- Subsequent studies will be made with BeO particulate.
- The prototype instrument will be built on a cart to make it more portable.